



Effect of ozonation on organic substance removal efficiency during adsorption

Małgorzata Wolska^{a,b,*}, Justyna Machi^a, Sławomir Szerzyna^a, Marek Mołczan^{a,b},
Wojciech Adamski^a, Jacek Wiśniewski^a

^aFaculty of Environmental Engineering, Wrocław University of Science and Technology, 27 Wybrzeże Wyspiańskiego st., 50-370 Wrocław, Poland, emails: malgorzata.wolska@pwr.edu.pl (M. Wolska), justyna.machi@pwr.edu.pl (J. Machi), slawomir.szerzyna@pwr.edu.pl (S. Szerzyna), marek.molczan@pwr.edu.pl (M. Mołczan), wojciech.adamski@pwr.edu.pl (W. Adamski), jacek.wisniewski@pwr.edu.pl (J. Wiśniewski)

^bWrocław Municipal Water and Sewage Company, New Technologies Centre, Na Grobli 14/16, 50-421 Wrocław, Poland

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ABSTRACT

The aim of the presented study was to evaluate the effect of the ozonation process before activated carbon adsorption on organic substance removal effectiveness and the adsorption process as a whole. The study was conducted in two flow-type water treatment systems: the reference and the test system. Both systems functioned continuously with a throughput of 3 m³/h, supplied by water uptake from Olawa River. Water was subjected to coagulation, sedimentation, rapid filtration, ozonation (reference system only) and adsorption. Such a configuration of processes allowed for a comparison of the effectiveness of organic substance removal during adsorption preceded by ozonation. Generally, the removal efficiency of dissolved organic carbon decreased with time since the study started, corresponding to decreasing bed adsorption capacity. The novelty of the research is the combination of chemical analysis with the microbiological aspect. Chemical transformations prove more effective in removing organic compounds by the use of the ozonation process before the activated-carbon filters. The assessment of the microbial content flushed into water indicates an increased development of biofilm in the reference system, which also intensifies the removal of organic compounds. The specific UV absorbance values after the adsorption process in both systems indicate the presence of organic substances of low molecular mass.

Keywords: Granular activated carbon filter; Organic matter; Microorganism; Ozonation; Water

1. Introduction

The presence of organic substances in natural water, especially surface water, may pose a serious hazard to human health, which has been repeatedly confirmed by studies worldwide [1–4]. This problem is aggravated by the identification of an increasing number of organic pollutants, particularly pharmaceuticals, cosmetics [5,6] and pesticides, whose consumption is increasing worldwide [7,8]. Apart from micropollutants, an ever increasing amount of residential and industrial sewage containing

organic substances of varying properties is being introduced into water [9–11].

These factors make it necessary to ensure highly effective removal of organic substances during treatment of water intended for human consumption. Consequently, an adsorption process is often included in conventional treatment processes [12,13], with the most common sorbent used being activated carbon [14,15]. This process, as shown by Hyung and Kim [16] allows for the removal of substances of low and medium molecular masses from water, which are susceptible to removal by coagulation to a low degree [17]. This enables a simultaneous increase in the effectiveness in removing micropollutants [18–20] as well as disinfectant

* Corresponding author.

by-product precursors [21]. Additionally, in the case of adsorption on activated carbon beds, a spontaneous bio-film formation occurs on the surface of sorbent grains [22], which enables biodegradation in addition to adsorption [23]. Often, this mechanism allows for a significant increase in organic substance removal effectiveness, including dissolved organic carbon (DOC) [24], while also increasing bed lifetime. Therefore, the novel combination of chemical and microbiological analysis will allow the evaluation of both mechanisms – adsorption and biodegradation of organic compounds.

An evaluation of the adsorption process showed that the parameters determining the course of this process, apart from carbon properties and the type of pollutants present in water, are the water-carbon contact time and the water temperature [25,26].

Many authors indicated that the effectiveness of the adsorption process in removing organic substances may be increased by the introduction of an ozonation process prior to adsorption [4,27,28]. This process allows for a transformation of organic matter from large molecular mass substances into those of a lower molecular mass [29], which makes them more susceptible to adsorption. However, there is no clear information concerning the effect of introducing ozonation prior to adsorption, and therefore, it was justified to conduct studies aiming to compare organic substance removal effectiveness in systems with and without ozonation prior to adsorption. Conducting studies in a flow-type system allowed for evaluating adsorption over time and monitoring the depletion of the adsorption potential of the activated carbon bed in both systems.

The aim of the research was to determine the effect of the ozonation process on the adsorption effectiveness and the “durability” of activated carbon by analyzing both chemical and microbiological changes.

2. Subject and methods of study

The study was carried out in flow water treatment systems (reference and test), consisting of coagulation, sedimentation, rapid sand filtration and adsorption (Figs. 1(a) and (b)). In one of the systems (reference) an ozonation process prior to adsorption was introduced, which allowed for an evaluation of organic substance removal effectiveness with and without ozonation prior to adsorption. Both systems operated continuously with a throughput of 3 m³/h. The system was supplied by surface water uptake by a water treatment plant.

The study was started after the adsorption filters of both systems were filled with fresh activated carbon (March 2017) and ran for 4 months.

The adsorption process was carried out on rapid filters filled with granulated activated carbon (WG12), whose properties are shown in Table 1.

Fresh activated carbon was inhabited by only individual live organisms, as was confirmed by a photograph of the fresh

Table 1
Properties of WG12 activated carbon^a

Nos.	Parameter	Value
1	Bulk density, g/L	470
2	Volatile substance content, %	1.50
3	Ash content, %	11.6
4	Specific surface area, m ² /g	968
5	Iodine number, mg/g	1,014
6	CTC – adsorption CCl ₄ , %	62.3
7	<0.5 mm subfraction content, %	0.0
8	Mechanical strength, %	97.3

^aData from the Gryfskand manufacturer (Poland).

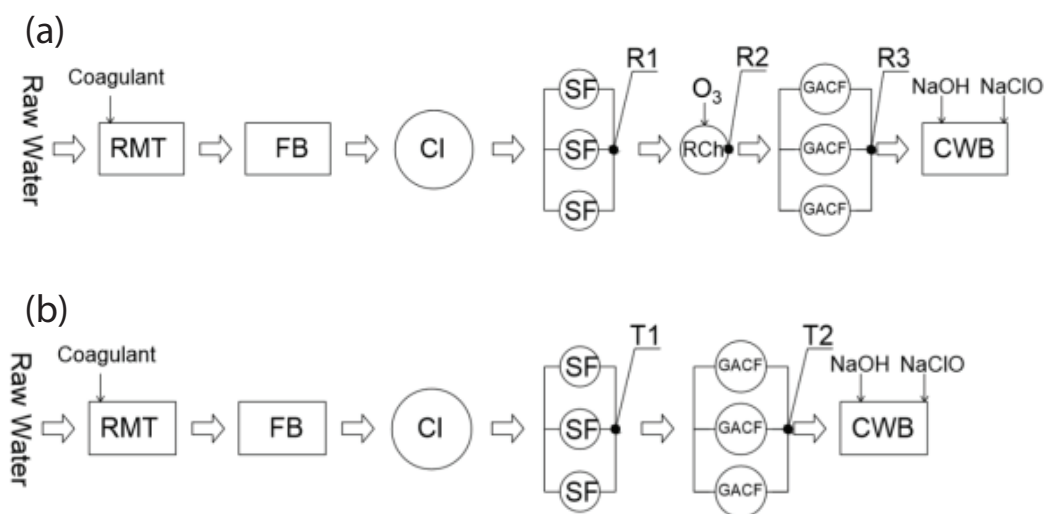


Fig. 1. (a) Schematic of reference water treatment system showing sampling points. RMT, rapid mixing tank; FB, flocculation basin; CI, clarifier; SF, sand filter; RCh, reaction chamber; GACF, granular activated carbon filter; CWB, clear water basin; sampling points: R1 – before adsorption and ozonation, R2 – after ozonation and R3 – after adsorption. (b) Schematic of test water treatment system showing sampling points. RMT, rapid mixing tank; FB, flocculation basin; CI, clarifier; SF, sand filter; GACF, granular activated carbon filter; CWB, clear water basin; sampling points: T1 – before adsorption and T2 – after adsorption.

carbon surface with the use of a live-dead dye (Fig. 2). The photo was taken under a fluorescence microscope.

The water-bed contact time for both systems was between 17 and 19 min. Insignificant changes in the flow time through the beds resulted from constant system throughput.

The ozonation process (reference system) was operated with a constant ozone dosage of 1.2 g O₃/m³, generated by a BMT 803 BT Ozone generator.

The objects of study were water samples before and after adsorption, and before ozonation (Figs. 1(a) and (b)). Samples were taken once a day from Monday to Friday. Water temperature, pH, alkalinity, specific conductivity and concentrations of oxygen, DOC, phosphates and ammonium were determined for all water samples. Additionally, the water turbidity was analyzed, along with color at wavelengths of 340 and 410 nm, and UV absorbance at wavelengths of 254

and 272 nm. Furthermore, the electrokinetic potential was measured once per week, which allowed for an evaluation of the stability of the colloid. The total psychrophilic microorganism count was also measured weekly, along with the total mesophilic microorganism count.

Based on the absorbance values of UV₂₅₄ and DOC, specific UV absorbance (SUVA) was calculated. All evaluations were performed according to applicable Polish Standards.

Due to the conducted study, it was possible to compare the effectiveness of the adsorption process in removing organic substances both with and without an ozonation process preceding adsorption. Additionally, the ozonation process influence on biofilm develop was analyzed. Changes in effectiveness with respect to input water quality were also evaluated. During the study period, significant changes in quality of the input water were observed due to changes of seasons, particularly because of changes in water temperature.

The aim of the research was to determine the effect of the ozonation process on the adsorption effectiveness and the “durability” of activated carbon by analyzing both chemical and microbiological changes.

3. Results

The water samples subjected to adsorption in both systems were characterized by a high variability in water quality indicators (Table 2), particularly those testifying to contamination with organic substances.

The dissolved organic content in 2.5% of water samples exceed the acceptable level for drinking water (under 5.0 mg/L), despite treatment during coagulation,

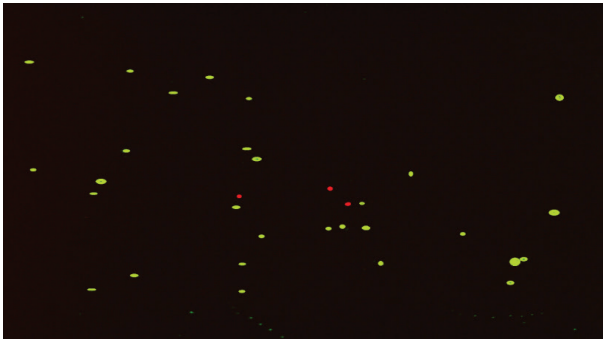


Fig. 2. Photograph of carbon surface with the use of a live-dead dye (green areas – live bacteria, red areas – dead bacteria).

Table 2
Water quality indicator ranges at individual sampling points

Parameter	T1	T2	R1	R2	R3
Temperature, °C	10.9–23.5	11–23.5	10.4–23.5	10.8–23.7	11.1–23.7
NH ₄ ⁺ , g	<0.05	<0.05	<0.05	<0.05	<0.05
NH ₄ ⁺ , m ³					
Turbidity, NTU	0.0–0.5	0.0–0.3	0.0–0.4	0.0–0.6	0.0–0.4
pH	6.94–8.16	6.94–8.26	6.88–7.76	6.81–7.81	6.62–8.17
Psychrophilic microorganisms, cfu/mL	65–310	15–4,100	24–850	0–260	180–260,000
Mesophilic microorganisms, cfu/mL	1–140	5–3,700	4–230	0–52	16–19,000
PO ₄ ⁻³ , g	0–0.27	0–2.40	0–0.21	0–0.20	0–2.40
PO ₄ ⁻³ , m ³					
Conductivity, μS/cm	383–734	7.6–740	383–735	384–735	386–743
DOC, gC/m ³	2.34–5.58	0.30–2.79	2.27–5.71	2.25–5.49	0.36–2.86
UV ₂₅₄ , m ⁻¹	5.1–12.2	0.0–5.3	5.1–12.6	1.7–9.1	0.0–3.9
UV ₂₇₂ , m ⁻¹	4.0–9.8	0.2–4.2	4.0–10.1	1.2–6.7	0.0–2.8
Alkalinity, val/m ³	1.88–3.57	1.9–3.6	1.85–3.58	1.85–3.57	1.89–3.58
Color 340, g/m ³	4.3–10.3	0.0–4.0	4.3–10.8	0.8–5.7	0.0–2.4
Color 410, g/m ³	6.0–13.6	0.0–4.7	3.0–14.2	0.8–6.8	0.0–3.0
Electrokinetic potential, mV	-7.55 to -2.39	-6.26 to -2.51	0	-9.68 to -3.1	-9.13 to -3.72
SUVA, m ³ /g·m	1.60–2.44	0.03–2.19	1.66–2.41	0.71–2.35	0.00–2.38

sedimentation and filtration processes. The increase in DOC concentration in water undergoing adsorption or ozonation with adsorption above 5 g C/m^3 took place in May (Fig. 3), and was connected with a sudden decrease in input water quality as a result of spring surface runoffs after intense rains [30].

Among the organic substances, ultraviolet radiation absorbing substances dominated, which is confirmed by the linear correlations that were found (Fig. 4). This indicated their large susceptibility to removal by adsorption [31].

Water undergoing ozonation and adsorption or adsorption was saturated with dissolved oxygen, which is a requirement for biofilm development on the surface of an activated carbon bed [32]. Food substrates present in water stimulates biofilm development [33].

The adsorption process ensured a significant decrease in organic substance content, and consequently decreased UV absorbance and color intensity (Table 3).

The highest removal efficiency of above indicators (90.20%–99.96%) was obtained at the beginning of research when granular activated carbon was fresh. At the same time, 85.2% of samples of water taken from the reference system showed higher removal efficiency of DOC than in the system without ozonation. In the remaining water samples, the effectiveness that was found was lower by a maximum of 2% and therefore did not exceed the error of analysis of DOC content. The effectiveness in removing DOC during the study period was greater by 17.9% and increased with increasing bed operation time.

In both systems, the effectiveness of reducing DOC concentrations decreased with increasing operating time of the filters, that is, with depletion of the activated carbon adsorption capacity (Fig. 5). Both of these relationships indicate a slower depletion of the bed capacity in the reference system. The differences were small, it is probably due to the intensified biodegradation associated with the presence of higher concentrations of biodegradable organic matter in water after ozonation [34]. It means that the ozonation had small influences on DOC removal during adsorption.

The effective elimination of organic matter also reduced the UV absorbance, both at 254 and 272 nm (Figs. 6(a) and (b)). As with DOC, this efficiency diminished with a prolonged operating time of the carbon bed filters. In the first month of activated carbon bed operation, differences in the UV_{254} and UV_{272} absorbance reduction effectiveness between the systems were small and were in the ranges of 7.7%–15.8% and 9.0%–18.2%, where the larger effectiveness was found in the system with ozonation. In the later period, the effectiveness of the reference system was much higher than that obtained in the test system. This may be influenced by: different susceptibilities of organic substances after ozonation to adsorption as well as a lower filter load in the reference system and the development of a biofilm on the bed surface. This may also be due to a decrease in UV absorbance during the ozonation process itself, which is confirmed by studies [35] and also due to the fact that the ozonation process allowed for a change in the organic substance structure, as has been confirmed by many studies [29,36,37].

Additionally, significant decreases in the UV_{254} and UV_{272} absorbance were observed during the ozonation process, with only a small decrease in DOC (Table 3). Structural

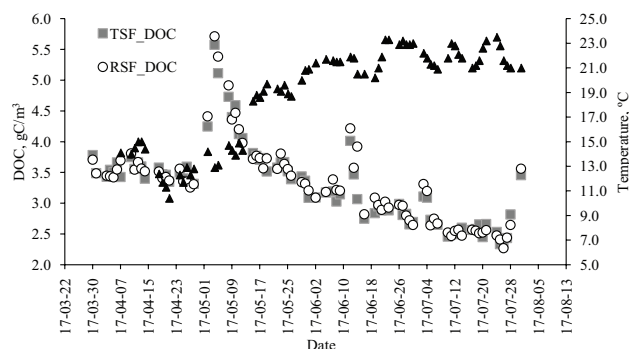


Fig. 3. Variation in dissolved organic carbon content in water supplying activated carbon bed filters.

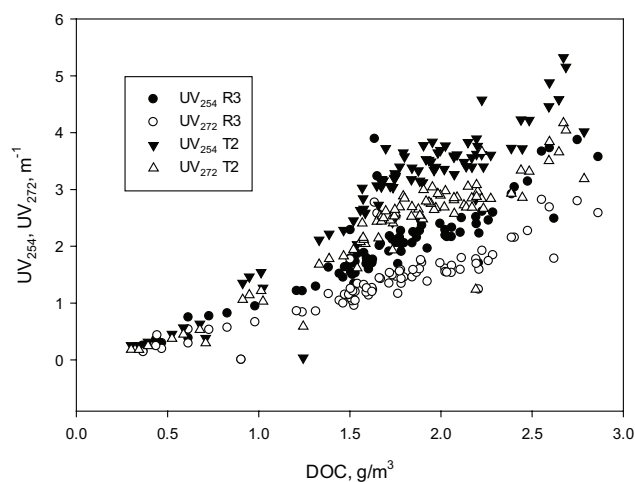


Fig. 4. Relationship between UV absorbance in water and dissolved organic substance content.

Table 3
Ranges of effectiveness in lowering selected water quality indicators

Parameter	Reference system	Test system
DOC, %	28.4–90.2	25.5–92.1
UV_{254} , %	40.5–96.8	37.2–99.4
UV_{272} , %	47.2–99.96	42.0–97.0
Color 340, %	56.4–99.7	49.9–99.7
Color 410, %	66.4–98.9	50.1–97.8

changes decrease the molecular mass of organic compounds, which makes them more susceptible to biodegradation, and influences susceptibility to adsorption to only a small degree. At the same time, a lower DOC concentration in water reaching adsorption filters, caused by DOC removal during the ozonation process, lengthens the adsorption cycle, slowing the adsorption front translation speed.

The use of ozonation before carbon filtration beds increases the concentration of organic food substrates for microorganisms inhabiting the activated carbon surface. Therefore, this causes an intensification in biofilm

development, as evidenced by the flushing of a larger number of microorganisms found in the reference system than in the test system (Fig. 7).

The very intense flushing of microorganisms during the first period of the study and its gradual decrease is a result of reaching the stabilization phase in the natural organism development cycle, with respect to the biofilm. This phenomenon took place in the reference system, even though the ozonation process not only had an oxidative effect, but also a disinfectant effect, thanks to which only individual organisms entered the activated carbon beds. This indicated a significant influence of the organic substrate content on the speed of biofilm development on the bed surface.

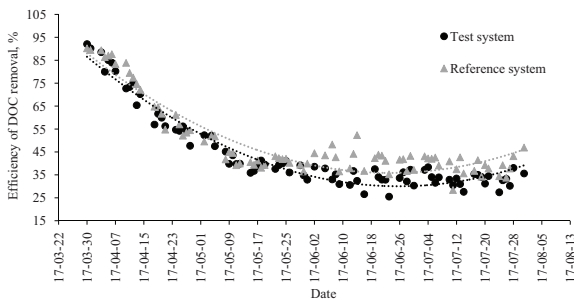


Fig. 5. Variation of DOC removal effectiveness in systems with and without ozone.

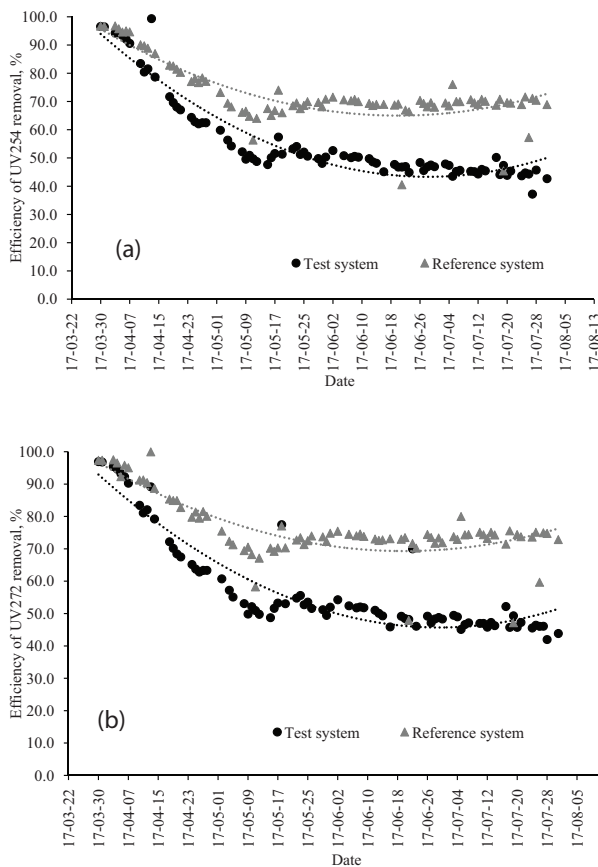


Fig. 6. (a) UV₂₅₄ absorbance reduction effectiveness. (b) UV₂₇₂ absorbance reduction effectiveness.

In the research system, the number of bacteria flushed into water was significantly lower, which is due to lower concentrations of organic food substrates in water reaching the filtration beds, and due to lower concentrations of ammonium ions, which are a ready source of non-organic nitrogen [38]. In both systems, phosphorus compounds were present in water undergoing adsorption, but its concentration was low, which could have been a factor limiting organism growth [39].

A decrease in UV₂₅₄ and UV₂₇₂ absorbance in both systems was almost proportional to the effectiveness in reducing color and DOC (Table 4), and consequently the reduction in absorption was greater in the system with ozonation (Table 3).

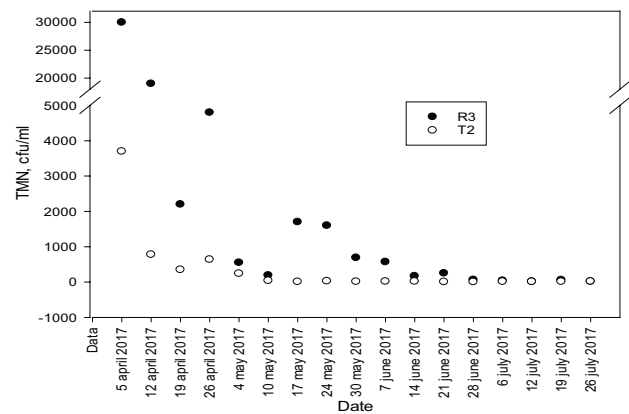


Fig. 7. Total number of mesophilic organisms in water after adsorption.

Table 4

Linear correlations between the reduction in DOC content and other water quality indicators

Correlation	R	Number of samples (system)
$\eta\text{DOC} = 1.0435 \cdot \eta\text{UV}_{254} - 14.374$	0.9662	81 (test)
$\eta\text{DOC} = 1.0611 \cdot \eta\text{UV}_{272} - 17.017$	0.9469	81 (test)
$\eta\text{DOC} = 1.2547 \cdot \eta\text{C}_{340} - 35.338$	0.9639	81 (test)
$\eta\text{DOC} = 1.3209 \cdot \eta\text{C}_{410} - 44.974$	0.9070	81 (test)
$\eta\text{C}_{340} = 0.8174 \cdot \eta\text{UV}_{254} + 17.51$	0.9853	81 (test)
$\eta\text{C}_{340} = 0.8389 \cdot \eta\text{UV}_{272} + 14.993$	0.9745	81 (test)
$\eta\text{C}_{410} = 0.7033 \cdot \eta\text{UV}_{254} + 28.038$	0.9428	81 (test)
$\eta\text{C}_{410} = 0.7312 \cdot \eta\text{UV}_{272} + 25.328$	0.9447	81 (test)
$\eta\text{DOC} = 1.3413 \cdot \eta\text{UV}_{254} - 48.664$	0.8722	80 (test)
$\eta\text{DOC} = 1.4014 \cdot \eta\text{UV}_{272} - 57.817$	0.8473	80 (reference)
$\eta\text{DOC} = 1.586 \cdot \eta\text{C}_{340} - 85.703$	0.7331	80 (reference)
$\eta\text{DOC} = 1.1259 \cdot \eta\text{C}_{410} - 52.365$	0.4644	80 (reference)
$\eta\text{C}_{340} = 0.592 \cdot \eta\text{UV}_{254} + 41.849$	0.8301	80 (reference)
$\eta\text{C}_{340} = 0.6562 \cdot \eta\text{UV}_{272} + 34.923$	0.8585	80 (reference)
$\eta\text{C}_{410} = 0.3858 \cdot \eta\text{UV}_{254} + 61.357$	0.6074	80 (reference)
$\eta\text{C}_{410} = 0.4474 \cdot \eta\text{UV}_{272} + 55.364$	0.6856	80 (reference)

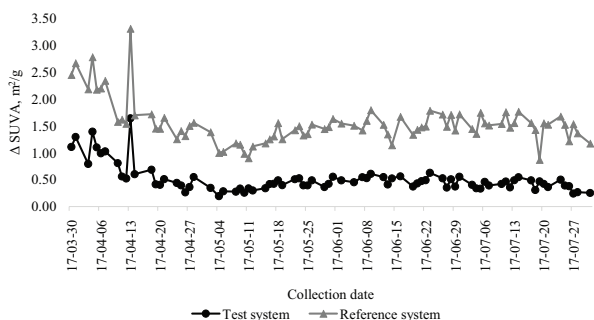


Fig. 8. Comparison of the variability in reducing specific absorbance in systems with and without ozonation.

A consequence from the reduction of organic substance concentrations, particularly those absorbing UV radiation, was a decrease in the SUVA, whose values in all water samples taken from the reference system after adsorption were lower than in water not undergoing ozonation. The reduction in SUVA in the reference systems in 96.3% of water samples was 130% greater than that found in the test system (Fig. 8). This is due to a significant reduction in SUVA during the ozonation process, which changes the structure of organic substances into one more susceptible to adsorption [33], which increases the effectiveness of this process in removing DOC. SUVA values in water after adsorption in both systems were small (Table 1), and their average values were 1.63 and 1.07 m²/g, respectively, for systems without and with ozonation. This values point to the presence of mainly substances of a low molecular mass in water after adsorption, and to an increase in the effectiveness of removing substances of medium and low molecular mass in the system with ozonation.

The use of the ozonation process allowed not only for a lowering of water quality indicators measuring organic contamination, but also a slower decrease in this effectiveness with time, improving the adsorption process stability. Consequently, thanks to ozonation, the bed operating time can be lengthened while maintaining a higher removal effectiveness in removing organic substances.

The values of electrokinetic potential ζ , both in water before and after the adsorption process, point to a lack of stability of the colloidal system of contaminants in water [40]. In water after adsorption, the potential values were closer to the isoelectric point. These changes were significantly higher in the system without ozonation, which is probably due to the presence of larger molecular mass substances in this water, and a lack of transformation of these substances during ozonation.

4. Conclusions

This study has shown that:

- Incorporation of the ozonation process prior to adsorption increased the effectiveness of removing DOC and, in particular, UV-absorbing substances, thereby lowering the health risks associated with the formation of disinfection by-products. But the differences in effectiveness were small, up to 10%.
- In the system with ozonation, bacterial growth was significantly greater.

- The ozonation process reduced the amount of bacteria in the water entering carbon beds.
- Thanks to the use of ozonation, the “lifetime” of activated carbon beds was lengthened, with the effectiveness in removing organic substances being reduced much more slowly with time.
- The effectiveness in removing organic carbon in both systems was directly proportional to the decrease in UV absorbance and color intensity.
- In the system with ozonation, organic substances of a low molecular mass were removed to a larger degree, which yielded a greater reduction in SUVA.
- The adsorption process preceded by ozonation changes the electrokinetic potential to a smaller degree, which may testify to a greater stability of the colloidal system.

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